Molybdenum-Catalysed and -Mediated Cycloaddition Reactions: Efficient Synthesis of Complex Products from 1-Oxa-1,3-dienes and Cyclotrienes or -tetraenes

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Molybdenum-mediated [6 + 2]-cycloaddition reactions of unsaturated ketones to cyclotri- or -tetraenes, e.g. cyclohepta-1,3,5-triene or cyclooctatetraene, proceed under very mild conditions, in high yields and with excellent stereoselectivity starting from the appropriate dicarbonylbis[η^4-(1-oxa-1,3-diene)]molybdenum complexes. The stereochemistry of the product arising from the reaction of dicarbonylbis[η^4-(5-methylhex-3-en-2-one)]molybdenum with cyclohepta-1,3,5-triene allows one to deduce a stepwise mechanism for this addition. The reactants are fused, as would be expected from an *exo*-type approach, thus indicating an intermolecular attack of the cycloheptatriene. Tungsten oxadiene complexes are effective in analogous reactions at somewhat reduced reaction rates. Catalytic cycloadditions are observed in several cases when 1−5 mol% of the highly reactive dicarbonylbis[η^4-(*R*-(+)-pinocarvone)]molybdenum is employed as the catalyst. Cycloadducts are formed diastereospecifically in most cases. When cyclooctatrienes are employed as reactants, a sequence of electrocyclization of the triene and subsequent [4 + 2]-cycloaddition occurs with high selectivity and efficiency, leading to a pentacyclic ketone. The product structure reveals an *endo*-type approach of the polyene in this case.

Transition metal complexes are well-established reactants in cycloaddition reactions, e.g. in [2 + 1]- and [4 + 2]-addition reactions of various carbene complexes[1a] and [4 + 4]-cycloadditions catalysed by nickel(0)/triphenylphosphane systems[1b]. Reactions of the [2 + 2 + 2][1c] as well as the [4 + 2 + 2] type[1d], specifically those employing bicyclo-[2.2.1]hepta-2,5-diene (norbornadiene) as substrate, have also been described[1b]. Furthermore, tricarbonylchrom-

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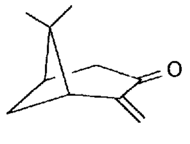
ium(0) complexes of cyclohepta-1,3,5-triene and its derivatives have been shown to react with electron-deficient alkenes and 1,3-dienes in [6 + 2]- and [6 + 4]-cycloadditions, respectively. Photochemical[2a] or thermal[2b] activation of the tricarbonylchromium(0) complexes is essential for these reactions to proceed at a reasonable reaction rate. Recently, a few examples of catalytic reactions of this type have been reported[3]. Reaction conditions, however, are rather drastic, i.e. temperatures above 130 °C are required, and about 9−15 mol% of the chromium complex is needed as catalyst. The topic of metal-mediated cycloadditions has recently been reviewed extensively[4].

It is the objective of this review to introduce a variety of molybdenum and tungsten η^4-oxa-1,3-diene complexes as reactants and catalysts for cycloaddition reactions in which several advantages such as mild reaction conditions, high yields and selectivities are combined. Considering the ease of preparation of the metal complexes, these reactions are of substantial preparative value.

Ligand Exchange in Bis(oxadiene)molybdenum and -tungsten Complexes

A variety of α,β-unsaturated carbonyl compounds such as unsaturated ketones, esters[5a] and amides[5b] can be transformed into oxa-1,3-diene molybdenum and tungsten complexes by simple standard complexation methods which have been described in detail[6,7]. According to an empirical rule, prochiral oxadienes give rise to the formation of C_1-symmetrical complexes consisting of a $M(CO)_2$ fragment and two oxadiene ligands that are coordinated to the metal from different enantiotropic faces. In contrast, C_2-symmetrical complexes of analogous overall composition are obtained from chiral oxadienes such as the α,β-unsaturated terpene ketones *R*-(+)-pulegone[7a] and *R*-(+)-pinocarvone (**1**)[7b]. In metal complexes formed from these molecules, both ligands are coordinated from the same diastereotopic face of the ligand (see Scheme 1 for a comparison). When ketone ligands are employed in the above-mentioned reactions, the bis(oxadiene) complexes are obtained diastereospecifically. The molecular arrangement of the ligands in the coordination sphere of the metal is illustrated in Figure 1 for the pinocarvone-molybdenum complex (**2**)[8]. According to expectations based on the evaluation of steric hindrance, the dimethylmethylene bridges are located in an outward position relative to the central metal atom.

The well-known η^4-oxadiene tricarbonyl iron complexes such as benzylideneacetone-tricarbonyliron(0) (**3**) are excellent starting agents for the complexation of a variety of ligands such as alkenes and dienes, e.g. cyclohexa-1,3-diene. In contrast bis(oxadiene)molybdenum and -tungsten compounds are inert towards ligand exchange with alkenes and dienes under standard conditions. Whereas with the iron complexes, solvent-stabilized η^2-alkene complexes of the type **4** have been shown[9] to be intermediates in the ligand exchange process (Scheme 2), a complementary reaction can be assumed to be operative when molybdenum and tungsten complexes are involved. On the basis of ligand-exchange investigations involving oxadienes and with the help of NMR exchange spectroscopy[10], it is probable that solvent-stabilized intermediates **5** with a ligand coordination involving lone-pair electrons on the heteroatom, i.e. oxygen, are essential for any exchange reaction taking place (Scheme 3). With respect to the thermodynamic stability of



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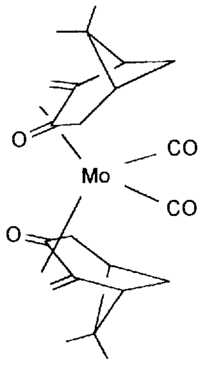

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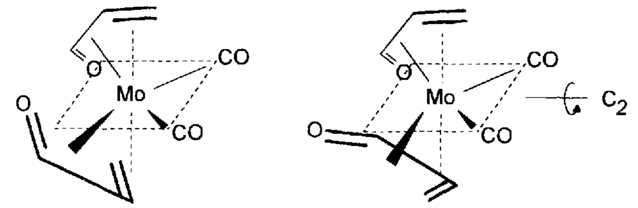
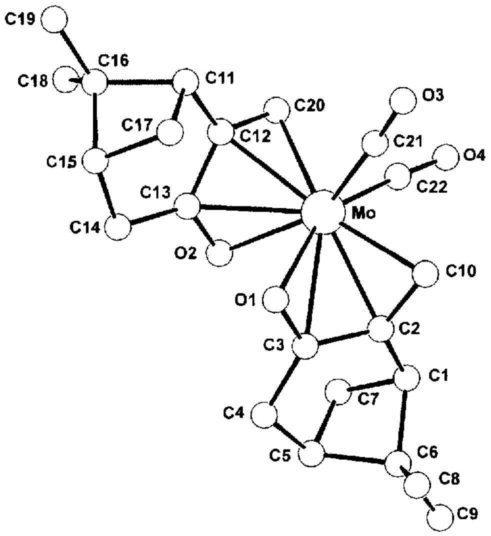
Scheme 1



C_1-symmetric complex of a prochiral oxadiene

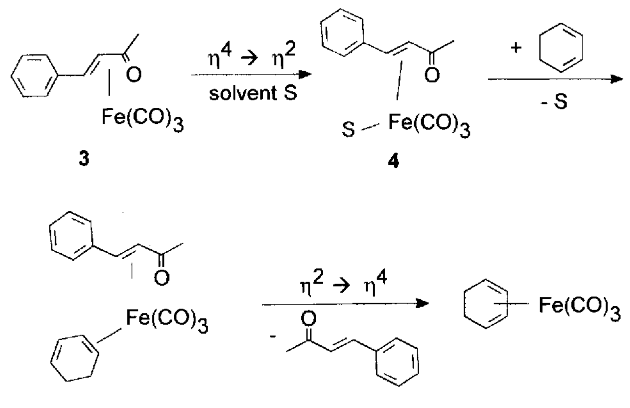
C_2-symmetric complex of a chiral oxadiene

Figure 1. Molecular structure of **2**; selected bond lengths [Å] and angles [°]: Mo−O1 2.263(4), Mo−O2 2.244(2), Mo−C3 2.421(3), Mo−C13 2.381(3), Mo−C2 2.260(3), Mo−C12 2.278(3), Mo−C10 2.254(3), Mo−C20 2.267(4), O1−C3 1.278(4), O2−C13 1.283(4), C2−C3 1.434(4), C12−C13 1.428(4), C2−C10 1.440(4), C12−C20 1.434(6), O1−C3−C2 118.7(2), O2−C13−C12 118.7(3), C3−C2−C10 115.7(3), C13−C12−C20 115.0(3), C21−Mo−C22 86.6(2), C10−C2−C3−O1 18.3, C20−C12−C13−O2 13.8

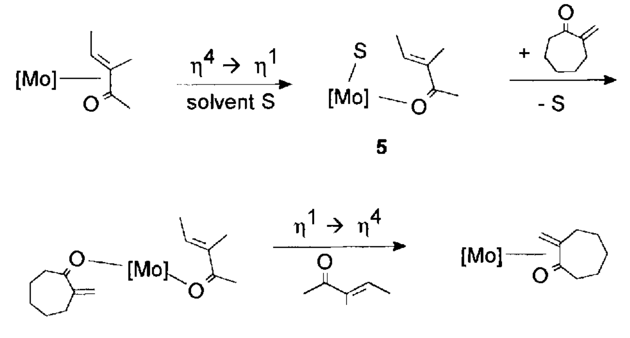


the products, an exchange hierarchy has been found, a part of which is shown in Scheme 4. For example, the 3-methyl pent-3-en-2-one complex **6** undergoes ligand exchange reaction with 2-methylenecycloheptanone to yield complex **7** almost quantitatively. Unsaturated compounds not containing heteroatoms are thus unable to participate in such exchange reactions due to the lack of lone-pair electrons at one of the coordinating centres. Similarly, lone-pair coordinated species have recently been shown to be intermediates in the diastereoisomerization of rhodium *N*-acyl amino acid complexes[11]. This observation additionally qualifies the oxadiene complexes as model compounds for such isomerizations.

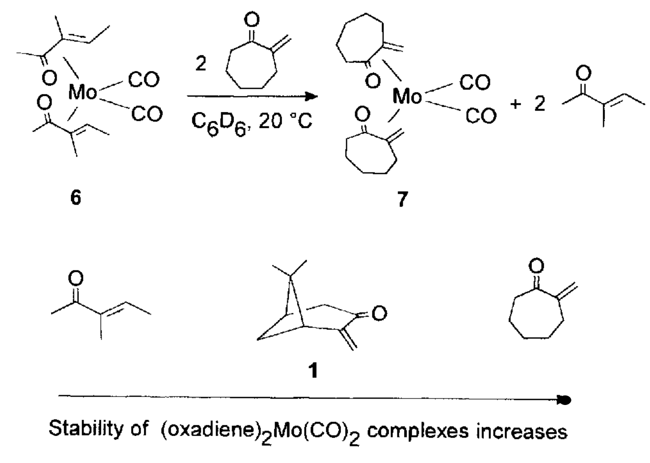
Scheme 2



Scheme 3



Scheme 4



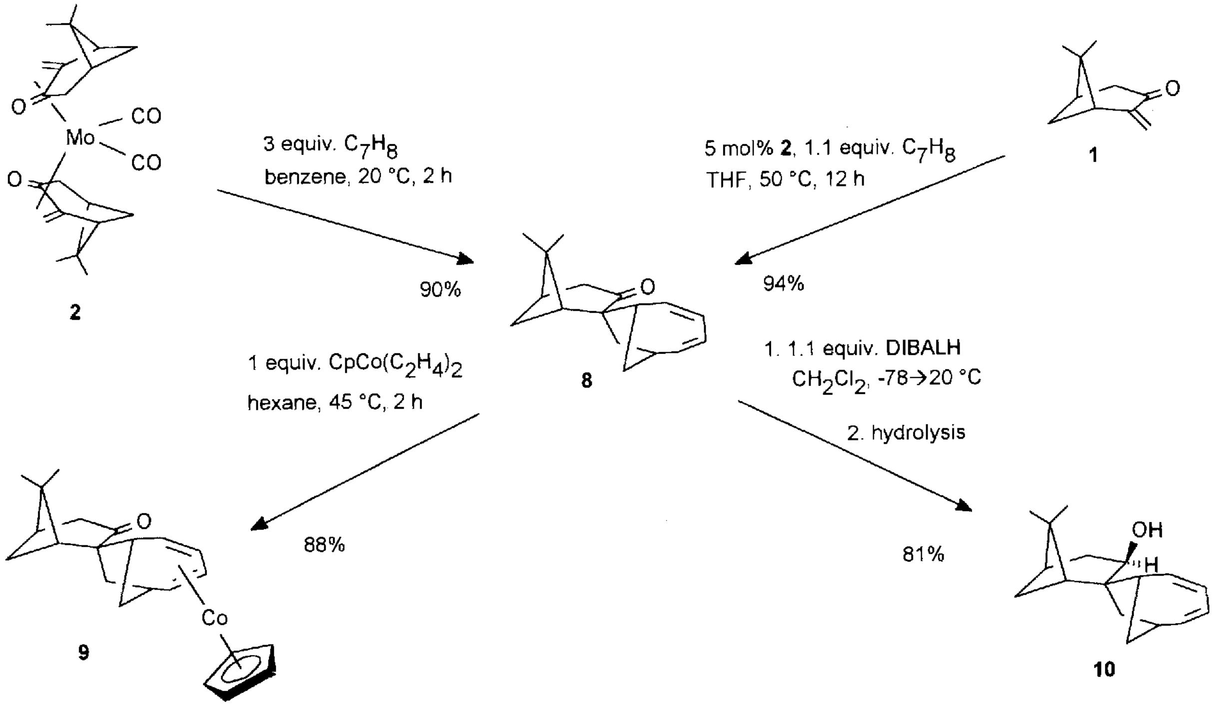
Stoichiometric [6 + 2]-Cycloadditions

In contrast to monoalkenes and dienes, cyclic tri- and tetraenes rapidly react with oxadiene molybdenum and tungsten complexes. For example, in the case of cyclohepta-1,3,5-triene and dicarbonylbis(η^4-pinocarvone)molybdenum(0) (**2**), this reaction takes place almost spontaneously even at room temperature, proceeding at comparable rate in polar (e.g. THF) and unpolar (e.g. cyclohexane) solvents and leading to the formation of tricarbonyl(η^6-cyclohepta-1,3,5-triene)molybdenum(0) as an organometallic and (1*R*,7*S*)-2,2-dimethyl[1,3:7,12]dimethanospiro[5,7]-trideca-8,10-dien-5-one (**8**) as the only organic product[8]. The latter is formed diastereospecifically and can be isolated in 90% yield after oxidative decomposition of the tricarbonylmolybdenum complex, either by stirring the reaction mixture in an atmosphere of air for several hours, or by treatment with an aqueous solution of cerium ammonium nitrate (CAN) until the yellow colour persists (Scheme 5). A similar, stoichiometric reaction takes place at slightly higher temperatures (30–40 °C) when the analogous pinocarvone tungsten complex is employed.

In order to establish the stereochemistry of the ketone **8**, two derivatives have been independently prepared because we were unable to obtain crystals of **8** that were suitable for X-ray crystal structure analysis. **8** has been shown to react with η^5-cyclopentadienylbis(η^2-ethene)cobalt(I) at 45 °C in *n*-hexane to yield 88% of the cobalt-diene complex **9**, which could be obtained in pure form by recrystallization from *n*-hexane (Scheme 5). Only one stereoisomer of the complex is formed in this reaction. According to the X-ray crystal structure analysis of **9**[12], the CpCo fragment approached the diene moiety from the outside of the molecule, i.e. away from the carbonyl group. In contrast, reduction of the carbonyl functionality in **8** by employing diisobutyl aluminium hydride in dichloromethane gives, after hydrolysis, an 81% yield of the secondary alcohol **10** (Scheme 5) as a crystalline, colourless solid. As is obvious from the molecular structure[13], shown in Figure 2b, the reduction of the ketone ocurred from the sterically less-hindered face of the carbonyl group, i.e. opposite to the dimethylmethano bridge, as would be expected from steric bulk considerations. Both reactions again proceed diastereospecifically, which implies that **8** may be a promising candidate for a synthetic building block on the way to bi- and polycyclic terpene-type target molecules.

A comparison of the structures of the starting complex **2** and the product derivatives **9** and **10** reveals important information about the cycloaddition mechanism. As the pinocarvone molecule is coordinated from the sterically less-hindered face of **2**, structures **9** and **10** prove that the cycloheptatriene approached this coordinated ligand exclusively from outside (*exo* attack according to Scheme 6), i.e. away from where the metal was originally located in the complex. A simultaneous activation of the alkene and the triene at the same metal centre, as has previously been assumed[2] for other metal-mediated [6 + 2]-cycloadditions, would be difficult to understand in the above case. The mechanism

Scheme 5



of the reactions reported here thus appears to be different from that of the chromium-mediated reactions.

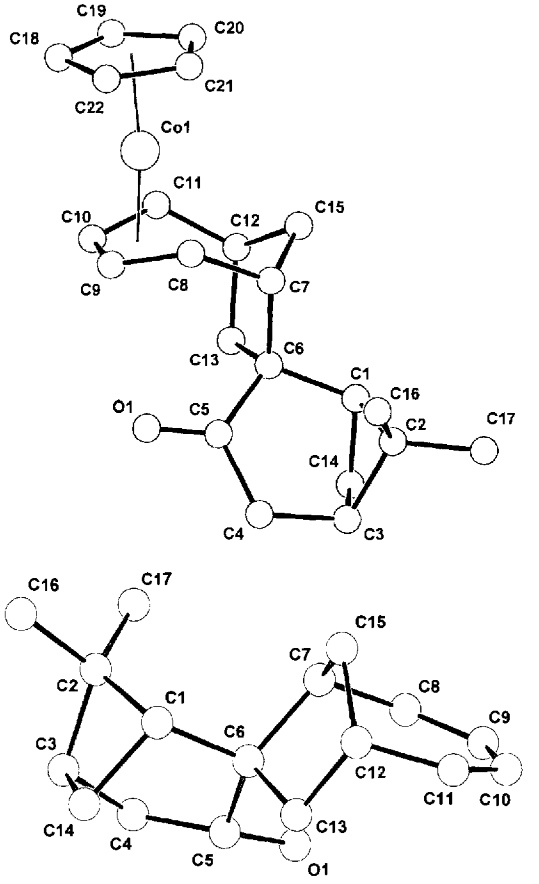
The molecular structures further reveal that the diene fragment of the triene moiety is oriented towards the oxygen atom of the alcohol **10** and therefore also the ketone **8**. This can be explained in terms of minimal steric hindrance during the approach of the cycloheptatriene to the oxadiene. It may be surmised that either a direct π-interaction between the diene and the ketone or a metal-mediated interaction, e.g. by chelating bonding of both the fragments, plays an additional role (Scheme 7) and could be responsible for the selectivity that is observed even in the absence of severe steric bulk.

As illustrated by the examples in Scheme 8, a variety of differently substituted bicyclo[4.2.1]nona-2,4-diene derivatives including spiro-fused compounds such as **12**[10] can be prepared by employing molybdenum complexes of prochiral oxadienes. Similarily, the geminally disubstituted derivative **14** is formed starting from complex **13**.

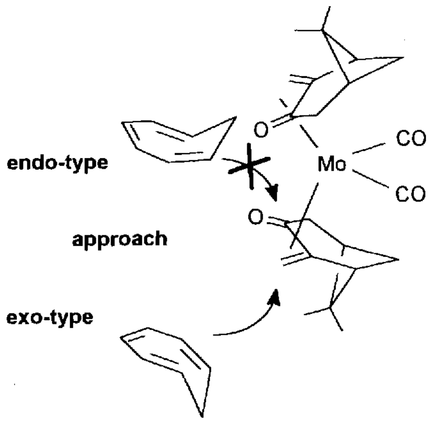
With a complex of an oxadiene alkylated in the β-position, e.g. the molybdenum complex **15** of (*E*)-5-methylhex-3-en-2-one, only a rather poor yield (34%) of a cycloadduct is obtained at the relatively high reaction temperature of 70 °C. Nevertheless, here again the product obtained was the only [6 + 2]-cycloadduct formed in the reaction. In other words, the cycloaddition itself again proceeds with a high selectivity (Scheme 9). The product **16**, originally assigned to contain the isopropyl and acetyl substituents in *trans* arrangement as shown in structure **17** on the basis of the *E*-stereochemistry of the starting material, has been subjected to X-ray crystal structure analysis, because of ambiguous results obtained from NMR investigations. From these data, a coupling constant $^3J_{HH}$ of about 10 Hz was found for the vicinal tertiary protons at the substituted carbons of the bicyclic ring system. In accordance with these results[14], the molecular structure determined (Figure 3) showed the two substituents to be in *cis* arrangement[15]. This can be taken as a clear indication for a stepwise mechanism of the reaction. A pathway as proposed in Scheme 10, tentatively assuming the intermediacy of ionic species, accounts for the observed selectivity. This does not exclude any other types of intermediates. In the stereochemistry-determining step, the preference for intermediate **18** can be understood in terms of the reduced steric hindrance compared with structure **19**, where the methylene bridge and the isopropyl group are located in close vicinity. The relatively rigid intermediate **20** benefits from additional electronic stabilization of the molybdenum centre by coordination with the pentadienyl moiety, which is accessible to the metal only after chain rotation brings H_a and H_b into *syn* position.

When cyclooctatetraene is employed instead of cycloheptatriene in the reaction with pinocarvone-molybdenum dicarbonyl complex, the stereoselectivity of the reaction is significantly reduced (Scheme 11). Two isomers of the cycloadduct are now produced in a ratio of about 3:1[16]. Although the stereochemistry of the product isomers, which are viscous oils at ambient temperature, has not been proven unequivocally by crystal structure analysis, it may be assumed that the major isomer has a structure similar to that of the cycloheptatriene adducts, i.e. the diene moiety should be in spacial vicinity to the ketone as shown for structure **21a**. As a reason for the lack of selectivity in this case, one may envision that both the diene and the monoene moiety serve

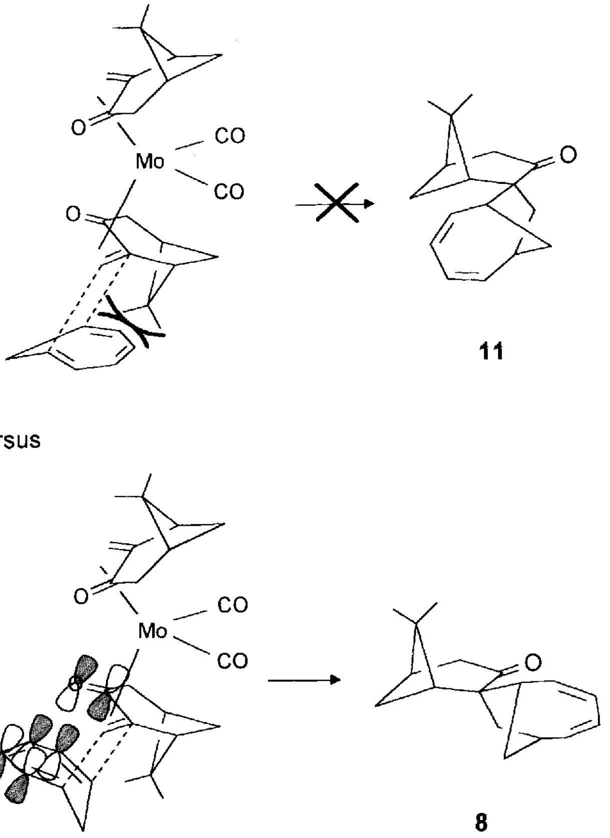
Figure 2. Molecular structures of cobalt(I) complex **9** (2a) and secondary alcohol **10** (2b); selected bond lengths [Å] and angles [°] for **9**: Co1–C8 2.046(3), Co1–C9 1.960(3), Co1–C10 1.961(3), Co1–C11 2.055(3), O1–C5 1.213(4), C4–C5 1.525(4), C5–C6 1.547(4); O1–C5–C6 122.2(3), O1–C5–C4 118.7(3); and for **10**: O1–C5 1.431(5), C5–C6 1.566(6), C6–C13 1.544(6), O1–C5–C6 115.0(3), C5–C6–C13 110.0(7), O1–C5–C6–C13 89.1(8)



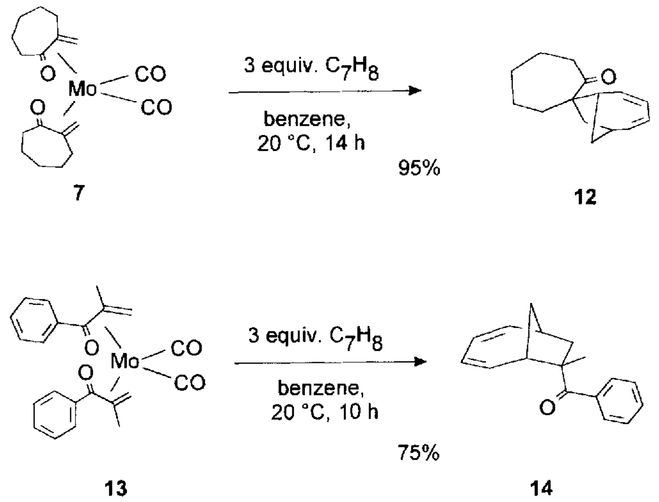
Scheme 6



Scheme 7



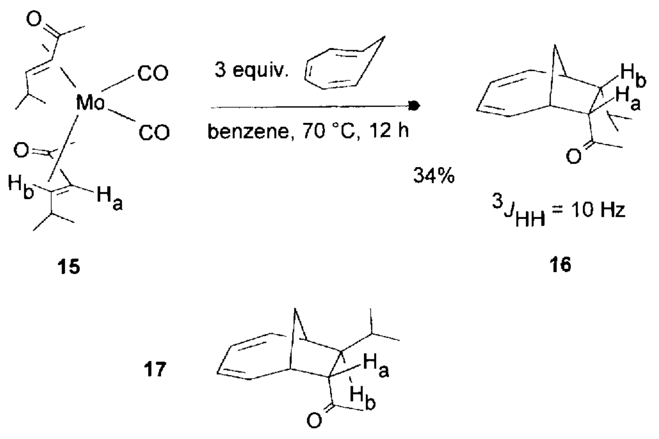
Scheme 8



as fragments capable of undergoing metal coordination in the course of the cycloaddition. In contrast, the analogous reaction of the 2-methylenecycloheptanone complex **7** leads to only one cycloaddition product **22**.

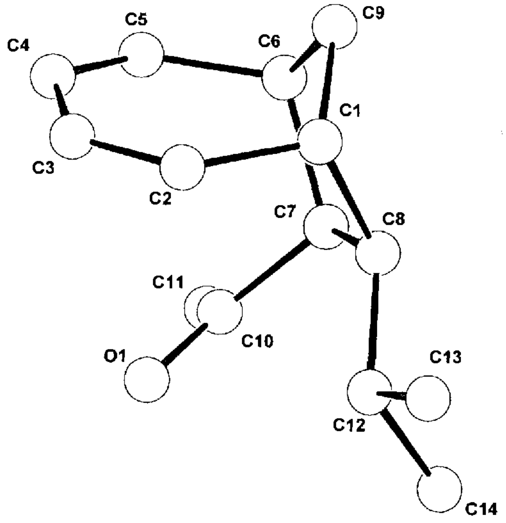
Mono-oxadiene complexes[17] containing additional donor ligands such as bidentate amines and phosphanes are also capable of undergoing the cycloaddition reaction[18]. These complexes of the general structure **23** are easily obtained from bis(oxadiene) complexes by ligand exchange with bidentate amine or phosphane ligands (Scheme 12). For the pinocarvone complexes yields of the mono-oxadiene complexes of 45–95% are obtained. From Figure 4, the distorted octahedral coordination geometry is obvious; this is typically observed for these yellow-brown to orange, almost air-stable complexes. For comparison, the cycloaddition reaction of the 2-methylenecycloheptanone complex

Scheme 9



24 to yield the adduct **12** is shown in Scheme 13. A longer reaction time and temperatures of about 70 °C are typically required for these reactions, indicating that the electron-enriched character of the central metal atom significantly slows down the reaction. This result additionally supports the mechanistic proposal of an initial nucleophilic attack of the polyene on the metal coordinate oxadiene, as proposed in Scheme 10.

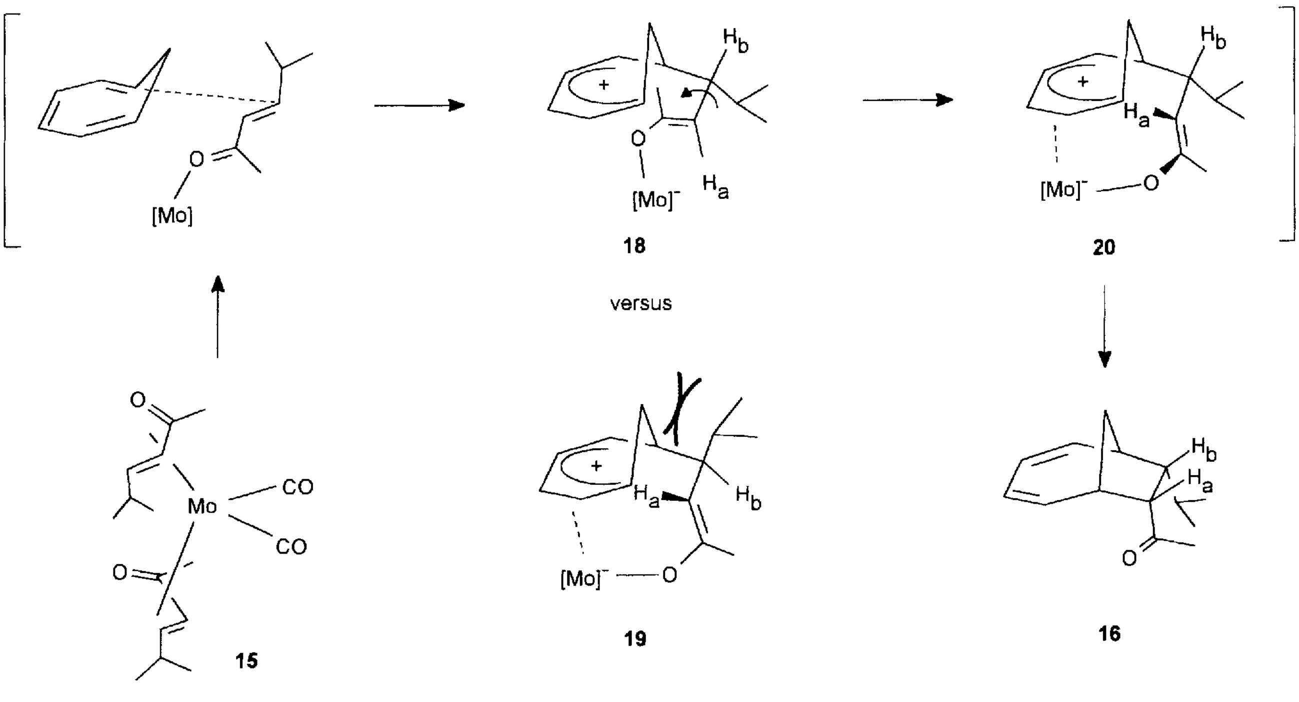
Figure 3. Molecular structure of cycloadduct **16**; selected averaged bond lengths [Å] and angles [°] from two independent molecules: C1–C2 1.491(3), C2–C3 1.324(4), C3–C4 1.458(4), C4–C5 1.324(5), C5–C6 1.490(4), O1–C10 1.214(3); C7–C8–C12 119.0(2), C8–C7–C10 119.0(2)



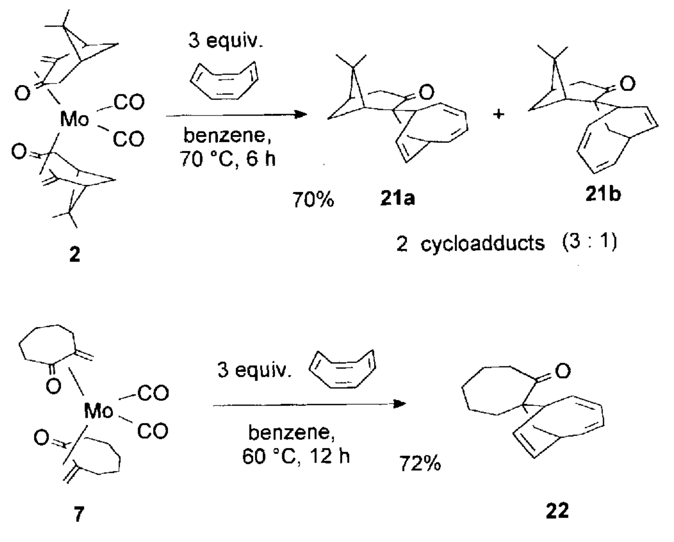
Catalytic [6 + 2]-Cycloadditions

Apart from the stoichiometric reactions reported so far, bis(oxadiene) complexes of molybdenum and tungsten may also function as catalysts for [6 + 2]-cycloadditions. In such a reaction, cycloadduct **8** can be obtained directly from pinocarvone (**1**) and cyclohepta-1,3,5-triene in the presence

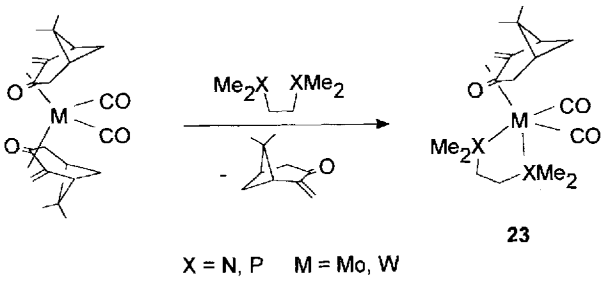
Scheme 10



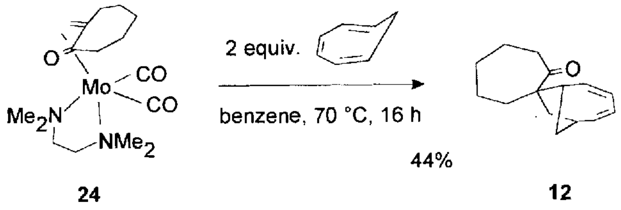
Scheme 11



Scheme 12



Scheme 13

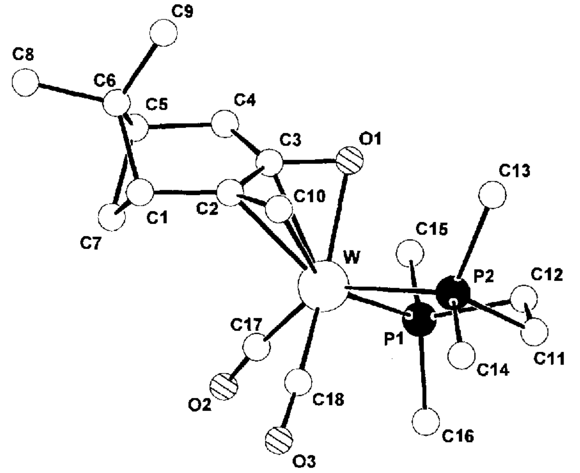


of 2–5 mol% of complex **2** at temperatures slightly above room temperature (Scheme 5)[7b].

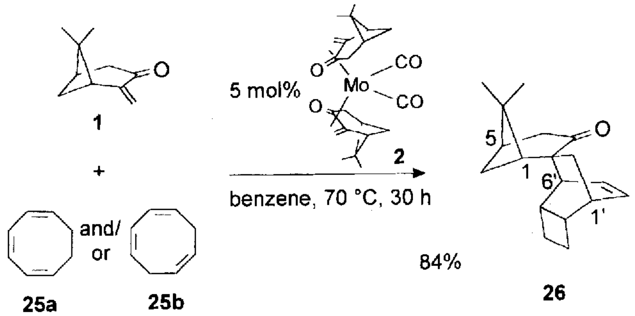
In the absence of the catalyst, no reaction was observed even at temperatures as high as 120 °C, where in fact pinocarvone already undergoes extensive thermal decomposition. Attempts to initiate a cycloaddition reaction by high pressure (13 kbar and up to 70 °C) or by the addition of Lewis acids such as titanium tetrachloride or aluminium trichloride were equally unsuccessful. Whereas no reaction at all occurred in the first case, decomposition and polymerization of the oxadiene took place in the latter case.

Catalytic reactions have been observed in several other cases so far, for example in the formation of the adducts **12** and **21** as well as in the cycloadditions of cycloheptatriene and pent-1-en-3-one or 1-phenylprop-2-en-1-one[18]. However, not all of the stoichiometric reactions shown above appear to be transferable into catalytic ones. The reasons for this behaviour remain to be investigated in more detail.

Figure 4. Molecular structure of mono-oxadiene complex **23** (M = W; X = P)[17]; selected bond lengths [Å] and angles [°]: W–O1 2.203(5), W–C3 2.304(6), W–C2 2.301(6), W–C10 2.261(7), W–C17 1.957(8), W–C18 1.910(8), W–P1 2.461(2), W–P2 2.505(2), O1–C3 1.307(7), C3–C2 1.430(9), C2–C10 1.41(1); W–O1–C3 77.4(4), P1–W–P2 77.49(7), O1–C3–C2 117.3(7), C3–C2–C10 117.2(7), C17–W–C18 77.4(4), O1–W–C10 73.6(3), P1–W–O1 85.8(1), P2–W–O1 90.5(1)



Scheme 14



As a preliminary hypothesis, the stability of the product complexes may be a limiting factor for catalysis, at least in the case of the cyclooctatetraene cycloadducts where relatively stable tricarbonylmolybdenum complexes of the bicyclo[4.2.2]nonatriene fragments are obviously formed, and these inhibit the transfer of the carbonyl molybdenum moiety to another substrate molecule.

Tandem Electrocyclization–Cycloaddition

In reactions employing cyclohepta-1,3,5-triene, [6 + 2]-cycloaddition has been demonstrated to occur uniquely. By the introduction of an additional methylene group into the cyclotriene, i.e. by using cycloocta-1,3,5-triene (**25a**), the course of the reaction is dramatically altered. With 5 mol% of the pinocarvone complex **2** used as catalyst, diastereoselective reaction of the triene with pinocarvone leads to the pentacyclic ketone **26** in 84% yield[19]. This can be isolated from the reaction mixture in the form of colourless crystals as the only organic product and is easily purified by recrystallization (Scheme 14).

The structure of **26** remained uncertain until the X-ray crystal structure analysis revealed its identity (Figure 5) as

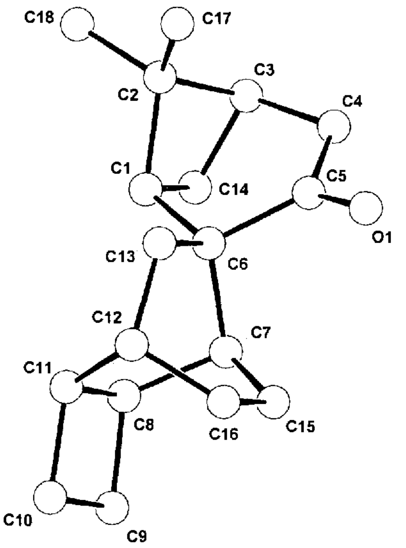


Figure 5. Molecular structure of the pentacyclic ketone **26**[19]; selected bond lengths [Å] and angles [°]: O1–C5 1.225(5), C15–C16 1.290(6), C1–C6 1.550(4), C5–C6 1.542(5), C6–C7 1.571(4), C6–C13 1.555(5); C6–C5–O1 120.1(4), C5–C6–C1 107.1(3), C5–C6–C7 107.2(3), C5–C6–C13 112.6(3), C1–C6–C13 111.0(3) (numbering scheme differs from that according to IUPAC rules)

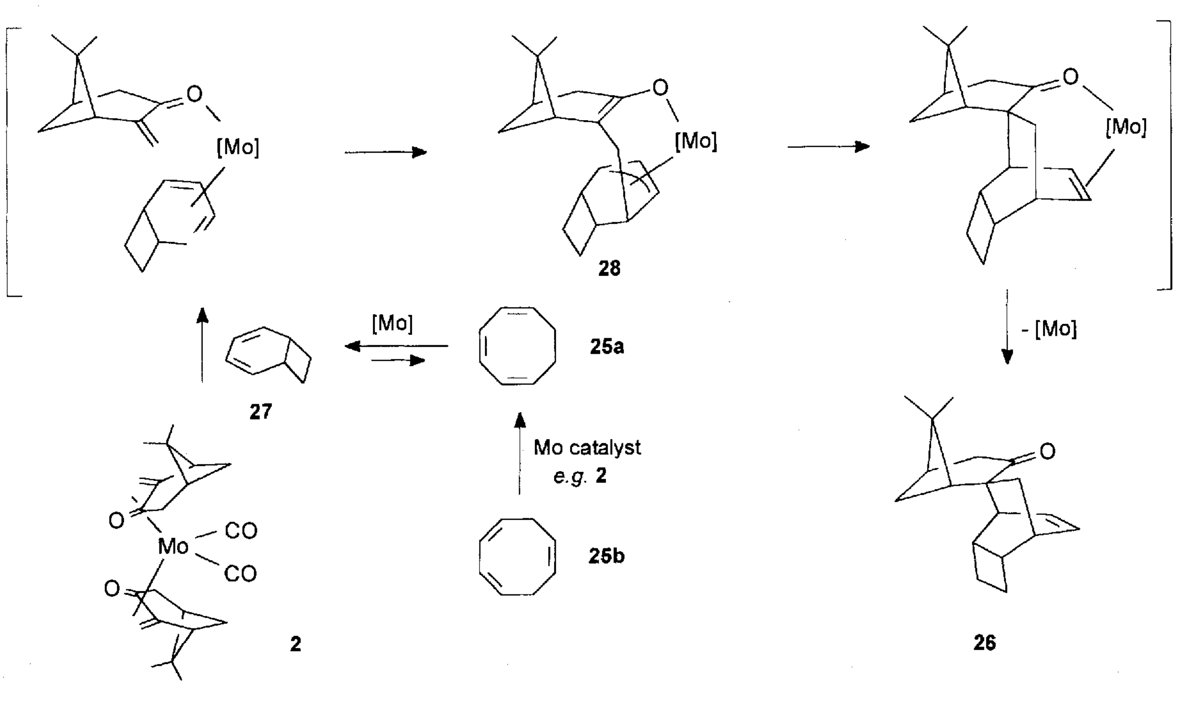
a formal [4 + 2]-cycloaddition product of an intermediate bicyclo[4.2.0]octa-2,4-diene (**27**). This bicyclic valence tautomer of the cyclotriene has of necessity to be formed in the coordination sphere of the catalytically active molybdenum atom. Therefore, and in contrast to the results obtained for the reactions with cycloheptatriene, where an *exo*-type addition takes place, the *endo*-type isomer is exclusively formed from cyclooctatriene. A mechanistic rationale for the formation of the product with the observed stereochemistry as shown in Scheme 15 basically requires an intramolecular pathway for the addition reaction. Thus, steric hindrance governs the orientation of the reactants coordinated to the same molybdenum centre for the first C–C bond formation. The primary intermediate is presumably bound to the metal centre in a bidentate mode. The molybdenum centre rigidly fixes this geometry and thus permits only one specific reaction pathway for the second C–C bond formation. After that, the product molecule remains coordinated to the molybdenum until it is liberated by ligand exchange with another reactant molecule, thereby closing the catalytic cycle.

Due to extensive catalytic properties of the molybdenum complexes involved, even cycloocta-1,3,6-triene (**25b**) can be employed in a similar reaction with comparable reaction rate and yield. As has been shown in separate, independent experiments, this is due to a rapid double-bond isomerization (**25b** → **25a**)[20] that takes place under the reaction conditions in the presence of various molybdenum(0) complexes. However, the oxadiene complexes such as **2** proved to be especially efficient in this reaction, even at relatively low temperatures. As a result, the nonconjugated cyclooctatriene or a mixture of 1,3,5- and 1,3,6-triene, as easily obtained from cycloocta-1,5-diene[21], can be employed in the cycloaddition reactions.

Conclusion and Perspectives

Molybdenum and tungsten complexes of 1-oxa-1,3-dienes have been shown to efficiently mediate and catalyse addition reactions of oxadienes and cyclopolyenes. Different stereo- and periselectivities can be realized, depending

Scheme 15



on the reactants employed. The reaction proceeds in a stepwise fashion and allows one to easily obtain complex polycyclic products in high yields and high isomeric purity. Future work directed towards the more precise elucidation of the mechanism of the various reactions should allow for a more precise prediction of product structures, making these cycloadditions into a valuable preparative tool, which is operable even under very mild reaction conditions.

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[8] The molybdenum complex **2** is isostructural to the analogous tungsten complex[7b] : X-ray crystal analysis of **2**[22] : Single crystal from *n*-hexane; 0.14 x 0.35 x 0.70 mm, Enraf-Nonius CAD4 diffractometer; Mo-K_α (graphite monochromator, λ = 0.71069), empirical formula $C_{22}H_{28}O_4Mo$, space group $C2$; unit cell dimensions: $a = 24.388(8)$, $b = 6.630(1)$, $c = 14.306(2)$ Å, $\beta = 117.59(1)°$; $d_{calc.} = 1.47\ g \cdot cm^{-3}$, $V = 2050.0(9)$ Å^3, $Z = 4$; μ (Mo-K_α) = 6.46 cm^{-1}, range for data collection $2\Theta_{max} = 64°$; ω scan; inex ranges: $-36 \leq h \leq 36, 0 \leq k \leq 10, 0 \leq 1 \leq 22$; reflections collected 3953; independent reflections 3824; parameters 245; no absorption correction. Structure solution: heavy atom method, structure refinement: Full matrix least-squares on F, $R = 0.026$, $R_w = 0.033$ based on 3693 reflections with $I > 2\sigma(I)$.

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[12] X-ray crystal analysis of **9**[22] : Single crystal from *n*-pentane; 0.18 x 0.25 x 0.49 mm, Enraf-Nonius CAD4 diffractometer; Mo-K_α (graphite monochromator, λ = 0.71069), empirical formula $C_{22}H_{27}CoO$, space group $P2_12_12_1$; unit cell dimensions: $a = 7.160(1)$, $b = 11.425(1)$, $c = 21.163(1)$ Å, $\alpha = \beta = \gamma = 90°$; $d_{calc.} = 1.41\ g \cdot cm^{-3}$, $V = 1731.3(1)$ Å^3, $Z = 4$; μ (Mo-K_α) = 9.93 cm^{-1}, range for data collection $2\Theta_{max} = 54.9°$; ω scan; index ranges: $0 \leq h \leq 10, 0 \leq k \leq 15, 0 \leq 1 \leq 28$; reflections collected 2302; independent reflections 2277; parameters 218; no absorption correction. Structure solution: heavy atom method, structure refinement: Full matrix least-squares on F, $R = 0.033$, $R_w = 0.044$ based on 2185 reflections with $I > 2\sigma(I)$.

[13] X-ray crystal analysis of **10**: Single crystal from methanol; 0.04 x 0,28 x 0.35 mm, Enraf-Nonius CAD4 diffractometer; Cu-K_α (graphite monochromator, λ = 1.54178), empirical formula $C_{17}H_{24}O$, space group $C2$; unit cell dimensions: $a = 15.037(2)$, $b = 16.465(2)$, $c = 12.702(2)$ Å, $\beta = 114.06(1)°$; $d_{calc.} = 1.13\ g \cdot cm^{-3}$, $V = 2871.4(6)$ Å^3, $Z = 8$; μ (Cu-K_α) = 4.85 cm^{-1}, range for data collection $2\Theta_{max} = 75°$; ω scan; index ranges: $-14 \leq h \leq 14, -14 \leq k \leq 14, 0 \leq 1 \leq 16$; reflections collected 6135; independent reflections 5867; parameters 324; no absorption correction. Structure solution: direct methods, structure refinement: Full matrix least-squares on $F, R = 0.055$, $R_w = 0.061$ based on 3714 reflections with $I > 2\sigma(I)$.

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[15] X-ray crystal analysis of **16**[22] : Single crystal from *n*-pentane/diethyl ether (9:1); 0.12 x 0.32 x 0.36 mm, Enraf-Nonius CAD4 diffractometer; Cu-K_α (graphite monochromator, λ = 1.54178), empirical formula $C_{14}H_{20}O$, space group $P1$; unit cell dimensions: $a = 8.034(1)$, $b = 10.682(1)$, $c = 14.952(1)$ Å, $\alpha = 102.41(1)°$, $\beta = 98.43(1)°$, $\gamma = 90.24(1)°$; $d_{calc.} = 1.10\ g \cdot cm^{-3}$, $V = 1238.8(2)$ Å^3, $Z = 4$; μ (Cu-K_α) = 4.80 cm^{-1}, range for data collection $2\Theta_{max} = 75°$; ω scan; index ranges: $-11 \leq h \leq 11, -14 \leq k \leq 14, 0 \leq 1 \leq 19$; reflections collected 5265; independent reflections 5077; parameters 271; no absorption correction. Structure solution: direct methods, structure refinement: Full matrix least-squares on F, $R = 0.055$, $R_w = 0.065$ based on 3618 reflections with $I > 2\sigma(I)$.

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